

Probe Segregation and T_g Determination of a Supported Ultra-Thin Polystyrene Film Studied by X-ray and Neutron Reflectivity, and SIMS

CHRIS WHITE* and WEN-LI WU

*National Institute of Standards and Technology
Polymers Division
Gaithersburg, MD 20899-8541*

YUXIE PU, M. RAFailovich, and J. SOKOLOV

*Stony Brook University
Stony Brook, New York*

Selective deuteration combined with X-ray and neutron reflectivity has been used to determine the extent of probe segregation to an interface in ultra-thin polymer films as a function of the number of thermal cycles. The extent of probe segregation to the interface was also investigated using Secondary Ion Mass Spectroscopy (SIMS). Significant probe segregation was not evident in these studies. X-ray reflectivity has also been employed to measure the coefficient of thermal expansion of ultra-thin polystyrene films supported on quartz. The glass transition temperature determined with this method is equivalent to that measured for bulk polystyrene films.

INTRODUCTION

The polymer physics literature has documented numerous examples of ultra-thin polymer films exhibiting physical behavior different from the behavior observed in the bulk. Assignment of the glass transition temperature (T_g) in the ultra thin films has been a common quest. Recent reviews (1, 2) state that T_g always decreases with decreasing film thickness for supported PS films, though there are still reports that do not conform to this generalization (3–6). However, the prevailing view is that the T_g of thin supported polymer films is reduced on a weakly interacting substrate and increased when the thermodynamic interactions are strongly favorable, as now demonstrated in several thin film systems (5, 7–12). This view is also supported by recent computer simulation studies (13–15).

Three recent fluorescent probe studies by Torkelson *et al.* demonstrated either a broadening in the distribution of α -relaxation times or a decrease in the assignment of T_g with decreasing film thickness (16–18). A separate study also using a different fluorescent

probe system exhibited no dependence of T_g on film thickness (19). Two major issues may account for the observed differences between these probe studies: the presence of local segregation of the freely diffusing local probes and the fact that these experiments were prepared on different substrates.

This paper examines these two issues in an attempt to explain the discrepancy between the two local probe studies. In the first section, the determination of the distribution of the chromophore throughout the spin cast film as a function of number of thermal cycles is assessed using two separate techniques: a combination of X-ray and neutron reflectivity measurements, and secondary ion mass spectroscopy (SIMS). In the second section, the T_g of the polystyrene films with the fluorescent probe supported on quartz substrate is determined by measuring the coefficient of thermal expansion with X-ray reflectivity.

Possible Chromophore Segregation

A critical consideration in any probe study is chromophore segregation. As stated in the **Introduction**, the prevailing view is that the T_g of thin supported polymer films is reduced on a weakly interacting substrate and increased when the thermodynamic interactions are strongly favorable, as now demonstrated

*Corresponding author.

in several thin film systems. If the chromophore segregates to a region that has a different T_g from that of the rest of the film, the fluorescence determination of T_g will primarily be based upon the measured dynamics of that layer and will not reflect the properties of the entire polymer film. One strategy to ensure a homogeneous distribution of the chromophores throughout the ultra-thin polymer film is to chemically bond the chromophore to the molecule of interest in either the backbone of the chain or as a side group (16–18).

In a previous fluorescent probe study, it was assumed that the probe, which was not chemically bound to the polymer, was not segregating during the experiment (19). In that study, the local dynamics were monitored by determining the configurational freedom of a chromophore, 1-3-bis-(1-pyrenyl)propane (BPP), that was present in the ultra-thin polystyrene spin cast films. The behavior of this chromophore system has been described in detail elsewhere (6, 20–22). Briefly, this chromophore fluoresces with two distinct wavelength ranges, I_{monomer} and I_{excimer} , which correspond to the different conformations of the molecule. The ratio of these two wavelength ranges indicates freedom of the chromophore to change configuration, which is a relative measure of the polymer's matrix viscosity. However, this flexibility of the chromophore can also present a potential caveat since it might possibly segregate to an interface of the polymer film.

In order to assess whether probe segregation occurred during these experiments, two reflectivity techniques (or one reflectivity technique with two different interrogation mechanisms), X-ray and neutron, were performed on a series of samples. X-ray reflectivity is sensitive to the electronic density versus the thickness of the material film, and neutron reflectivity, sensitive to the scattering-length density, is a property of the nucleus versus the thickness of the material film. By selectively deuterating either the chromophore or the polymer, a difference in the scattering length densities of these two components is introduced without significantly affecting the electron density. Creating this scattering length density contrast between the polystyrene and the BPP by selective deuteration allows for the determination of the relative position versus the thickness of each component within the film. If one of the components is segregating to an interface with no change in the overall film geometry, this segregation will be evident by observing no change in the parameters employed to generate the electron density model (X-ray). However, there will be a change in the parameters used to create the neutron scattering-length density model.

A comparison of the thickness and interfacial roughness employed to construct the best-fit models for both X-ray and neutron reflectivity data will provide an estimate of the extent of segregation of the hydrogenated component. In principle, either the BPP or the polystyrene could be selectively deuterated; in this study, the polystyrene was the deuterated component.

An example of the predicted sensitivity of the neutron reflectivity technique to a small degree of segregation is shown in Fig. 1. This figure illustrates the predictions of h-BPP segregation from a deuterated polystyrene matrix. The predictions of a uniformly mixed 40 nm film with a 10% mass fraction of BPP and 90% deuterated PS is shown as a solid line. This film has a roughness of 1 nm on both the top and bottom surfaces, a typical roughness encountered in experimental data. BPP segregation can be modeled by increasing the roughness of the top and bottom layer, and the predictions of reflected intensity versus q show significant deviations from the unsegregated film. These observations illustrate the excellent sensitivity of selective deuteration in neutron reflectivity. The corresponding plot of X-ray reflected intensity versus q predictions would show a very small difference as a function of BPP segregation induced roughness.

Secondary Ion Mass Spectroscopy (SIMS) has also been employed to determine possible chromophore segregation. In this technique, the ability to distinguish between the surrounding polymer matrix and the chromophore is again based on the selective deuteration of the polymer. By monitoring the C-H and C-D ratio, the relative abundance of the chromophore as a function of depth can be determined.

Possible Substrate Effects

A second possible explanation for the observed difference in the probe studies is the difference in chemistry of the supporting substrates. Previous studies have shown that this may have a large effect on the assignment of T_g (5, 23). In one of the probe studies (19), the measurements were performed on polystyrene films supported on a quartz substrate. The majority of the other studies were performed on a silicon substrate. In order to determine if the change in substrate is attributable for the difference between the probe studies, a series of X-ray reflectivity measurements of the coefficient of thermal expansion have been performed for a sample of polystyrene/fluorescent probe on a quartz substrate.

SAMPLE PREPARATION

Chromophore Distribution Experiment

A solution of d-polystyrene (synthesized by S. Smith, $M_n = 260,000$ g/mole) in toluene was prepared with mass fraction 0.0112 ± 0.0004 . (Throughout this article, quoted uncertainties represent the best estimate of two standard deviations in the experimental uncertainty (24)). A mass fraction of 0.1 BPP/d-polystyrene was added to this solution. It was allowed to stand for 24 h before the films were spin cast. Four 10-cm-diameter single crystal silicon wafers were identically cleaned by exposure to an oxygen plasma (Plasmaline (25)) for 15 min followed by immersion in a buffered oxide etch solution for 2 min. The wafers were then rinsed with 18 M Ω water and placed in a UV/ozone cleaner for 3 min (Jelight #42 UVO). The films were

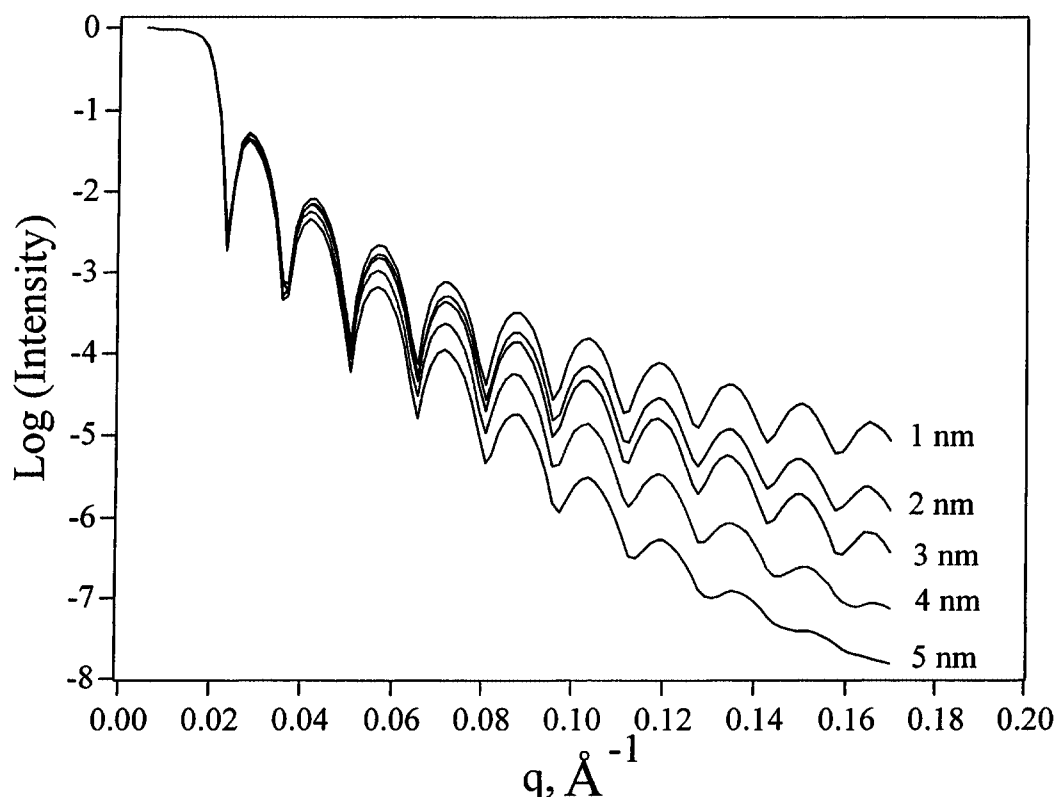


Fig. 1. Neutron Reflectivity Predictions. These intensity versus q predictions illustrate the sensitivity of this technique to chromophore segregation. The predictions are based on a 40 nm polymer film composed of deuterated polystyrene with a mass fraction of 0.1 hydrogenated BPP chromophore. The solid line is the prediction with no segregation to the top surface. The solid, dotted, broken, dashed, and long dashed lines are the predictions if segregation to the free surfaces causes an increase in the roughness to 1.0 nm, 2.0 nm, 3.0 nm, 4.0 nm, and 5.0 nm of the film, respectively.

spin cast onto the cleaned wafer surfaces within 20 min of the final UV/ozone cleaning. A Headway Spin Coater was used to spin cast the ultra-thin polymer films. The thickness of the film was set by the concentration of the polymer solution, and was (40 ± 3) nm for all four wafers.

The four wafers were processed for 0–3 thermal cycles inside a vacuum oven. Each thermal cycle consisted of heating the samples from 50°C to 130°C at a rate of 0.25°C/min. This was followed by immediately cooling the samples from 130°C to 50°C at a rate of –0.25°C/min. This thermal cycle was designed to be equivalent to that employed in a previous fluorescence determination of the T_g . A wafer was removed from the oven at the conclusion of each cycle to yield a set of samples with a thermal history of 0, 1, 2, 3 thermal cycles.

SIMS

A second set of samples was prepared for the SIMS experiment. Two 7.5-cm-diameter single crystal silicon wafers were cleaned with the above-described technique. Two solutions of d-polystyrene (Synthesized by S. Smith, $M_n = 260,000$ g/mole) in toluene were prepared with mass fraction 0.0132 ± 0.0004 .

To one of these solutions, a mass fraction of 0.1 BPP/d-polystyrene was added. Both solutions were allowed to stand for 24 h before the films were spin cast. A film of the d-polystyrene with BPP was spin cast onto a silicon wafer. This film was then floated off the surface of the silicon wafer onto 18 M Ω water. A film of d-polystyrene without the BPP was then spin cast onto a 7.5-cm-diameter wafer. The d-polystyrene layer without the BPP was then floated on top of the spin cast polymer film of d-polystyrene with BPP. These samples were then annealed at 70°C for 60 min and then 75°C for 30 min, and 0–3 of the above described thermal cycles. Post annealing, an approximately 22-nm-thick layer of dPS was floated on top of the samples. This sacrificial layer was needed in order to establish steady state sputtering conditions in the SIMS analysis.

Thermal Expansion Coefficient

Solutions of polystyrene (Polymer Laboratories Ltd., $M_n = 220,500$ g/mole, $M_w/M_n = 1.02$) in toluene were prepared with mass fractions of 0.0083 and 0.0046. BPP was added to this solution, such that a constant mass ratio of 0.1 BPP to polystyrene was maintained for both solution concentrations. These

solutions were prepared at least 24 h before the films were spin cast. The quartz disks (2.5 cm diameter) were washed in acetone, exposed to an oxygen plasma (Plasmaline) for 15 min, and placed in a UV/ozone cleaner for 3 min (Jelight #42 UVO). The films were spin cast onto the cleaned quartz disks within 20 min of the final UV/ozone cleaning. These films on quartz supports were annealed under vacuum for 12 hours at 150°C to remove residual solvent.

EXPERIMENTAL PROCEDURE

Chromophore Distribution

The thickness, roughness of both the top and bottom interfaces, and electron density was determined by X-ray reflectivity on a Scintag (XDS 2000) for the four samples with 0–3 thermal cycles. This technique involves experimentally determining the intensity of the reflected X-rays as a function of the scattering vector, $q = 4\pi/\lambda (\sin \theta)$, where λ is the wavelength and θ is the specular reflection angle, and determining the properties by constructing a model electron density profile. This model profile prediction is then compared to the experimental data of the specular reflected intensity versus q . The model is then modified until a satisfactory match of the experimental data and model prediction is achieved. The experimental thickness, roughness, and electron density of the ultra-thin polymer films is assumed to be identical to the model layer. The details of this technique are presented elsewhere (6, 22). The thickness was determined

with a standard uncertainty of ± 0.2 nm. This estimate of the uncertainty in the thickness is achieved by making small perturbations in the model predictions to generate a 10% increase in the chi-squared of the fit of the model predictions to the experimental data. The experimental data, calculated model fit, and electron density model are shown for the (40.1 ± 0.2) nm polystyrene film in Fig. 2.

Additionally, the reflected intensity versus q was determined by neutron reflectivity for these four samples on the NG7 beam line at the National Institute of Standards and Technology Cold Neutron Research Facility in Gaithersburg, Maryland. This is a similar technique to X-ray reflectivity, with a beam of highly collimated cold neutrons interrogating the sample instead of X-rays. The four wafers with attached ultra-thin polymer films were measured at ambient temperature. A scattering length density model was then fit to the experimental data by the same procedure used for X-ray reflectivity.

SIMS

The concentration profiles of the chromophores were detected using dynamic secondary ion mass spectrometry (SIMS). The concentration profiles of the chromophores were obtained with an Atomika 3000 SIMS by detecting negative ions sputtered by a 2keV Ar^+ beam incident at 30° off the sample normal to the surface and rastered over a $0.5 \text{ mm} \times 2 \text{ mm}$ area. The chromophore concentration was obtained by detecting the CH- and C-concentration profiles. The background

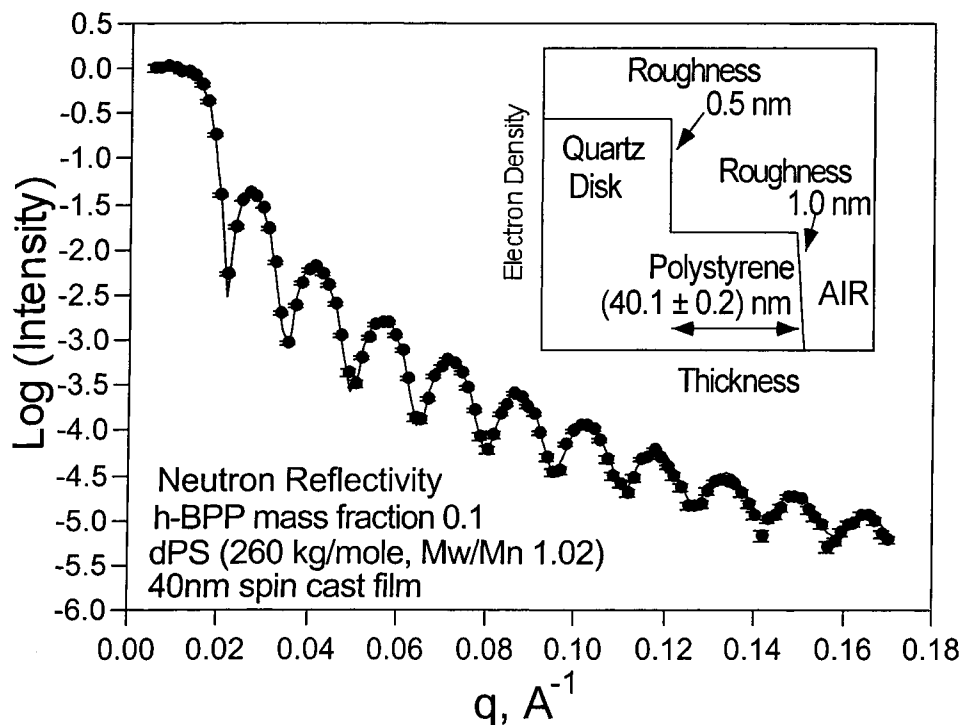


Fig. 2. Typical X-ray reflectivity data, including the model electron density profile and its corresponding prediction for intensity versus q are shown. The bars on the data points represent the standard uncertainty of the data points.

intensity was obtained by subtracting the C^{13} deduced from the natural abundance of the isotope in the C^{12} spectra. The depth calibration was obtained from independent measurements of the film thickness using ellipsometry and X-ray reflectivity. The depth resolution, as calculated from the carbon/SiO interface, is 80 Å. The details of the SIMS analysis have been described elsewhere (26).

Coefficient of Thermal Expansion

The X-ray reflected intensity versus q was determined for each polystyrene film on a quartz substrate for the temperature range of 20°C to 170°C. Each quartz sample was placed on the sample stage and enclosed inside a vacuum hood. Each film on quartz sample was then held under vacuum for 12 h at 150°C. Following annealing, the X-ray intensity versus q was determined. The temperature set-point was then reduced by 10°C, followed by a waiting period of 45 min to establish thermal equilibrium. The X-ray reflected intensity versus q was again determined. This procedure was repeated for the temperature range of 150°C to 20°C and then back up to 170°C, each procedure by 10°C increments. The measured X-ray reflected intensity versus q was fitted to a model electron density profile prediction for each temperature measurement in a similar method as described in the chromophore distribution experimental section.

RESULTS AND DISCUSSION

Chromophore Segregation

Typical X-ray intensity versus q data, including the model electron density profile and its corresponding prediction for intensity versus q , are shown in Fig. 2 for a 68 nm film. Similar data and predictions were obtained for the neutron intensity versus q for all four samples with different numbers of heating cycles. The parameters employed for the model fit for each sample are listed in Table 1 for both X-ray and neutron reflectivity curves. The X-ray data in this table show no change in the thickness or roughness as a function of number of thermal cycles, indicating that the heating and cooling cycles did not affect the overall film geometry. The roughness and thickness employed in the best fits for the neutron reflectivity data are also listed in Table 1. There is no appreciable change in roughness or thickness as a function of number of thermal

cycles. This is further illustrated in Fig. 3 by the neutron reflectivity intensity versus q data for 0, 1, 2, and 3 thermal cycles. Overlaying these four curves yields a single master curve.

The agreement between the neutron and X-ray reflectivity best fits to the data presented in Table 1 is within experimental uncertainty. The estimates of the uncertainty quoted in Table 1 are achieved by making small perturbations in the model predictions to generate a 10% increase in the chi-squared of the fit of the model predictions to the experimental data. This comparison of best-fit parameters between X-ray and neutron data, although straightforward in principle, is usually more difficult in practice. The X-ray parameters listed in Table 1 are used to construct an electron density model, and the neutron parameters are used to construct a neutron scattering length density model. While similar, these two thin-film models are not identical. The two techniques give similar values for the thickness and roughness, within the experimental error. This comparison, combined with the observation of no increase in roughness or decrease in thickness as a function of the number of thermal cycles, demonstrates that the probe is not significantly segregating to either the top or bottom surface during the heating and cooling cycles.

The value of the Q_c^2 (square of the scattering length density multiplied by 16π) is one further indication that the chromophore is not segregating. This value is sensitive to the composition of the film. The value employed in the best fit to the neutron reflectivity data is consistent with a BPP mass fraction of 0.1 (within the relative standard uncertainty $\pm 5\%$). In the X-ray data, the Q_c^2 values for the chromophore and the polystyrene are indistinguishable.

SIMS

Figure 4 shows the volume fraction versus depth profiles for the chromophore containing unannealed bilayers and those annealed for 70°C for 60 min, 75°C for 30 min, and the 4 thermal cycles (previously described). From this figure we can see that BPP chromophore diffuses gradually into the DPS layer. The diffusion constant for this size probe is estimated from additional studies employing a 1,8 dibromopyrene diffusing into hydrogenated polystyrene at $D = 5 \times 10^{-7} \mu\text{m}^2/\text{min}$ (19). These studies have additionally shown that there was no center of mass motion of the

Table 1. The Parameters Used To Compose the Best-Fit Models to the Experimental X-Ray and Neutron Reflectivity Data.

	Thickness Determined by X-ray ± 0.3 nm	Roughness (Si/Polymer Interface) ± 0.5 nm	Roughness (Polymer/Air Interface) ± 0.5 nm	Thickness Determined by Neutron ± 0.3 nm	Roughness (Si/Polymer Interface) ± 0.5 nm	Roughness (Polymer/Air Interface) ± 0.5 nm
As Spun	40.6 nm	1.2 nm	0.5 nm	40.3 nm	0.5 nm	0.5 nm
1 Heat/Cool Cycle	40.1	1	0.5	39.9	0.5	0.5
2 Heat/Cool Cycle	40.4	0.5	0.5	40.2	1.5	0.5
3 Heat/Cool Cycle	40.1	0.5	1	40.1	1.5	1

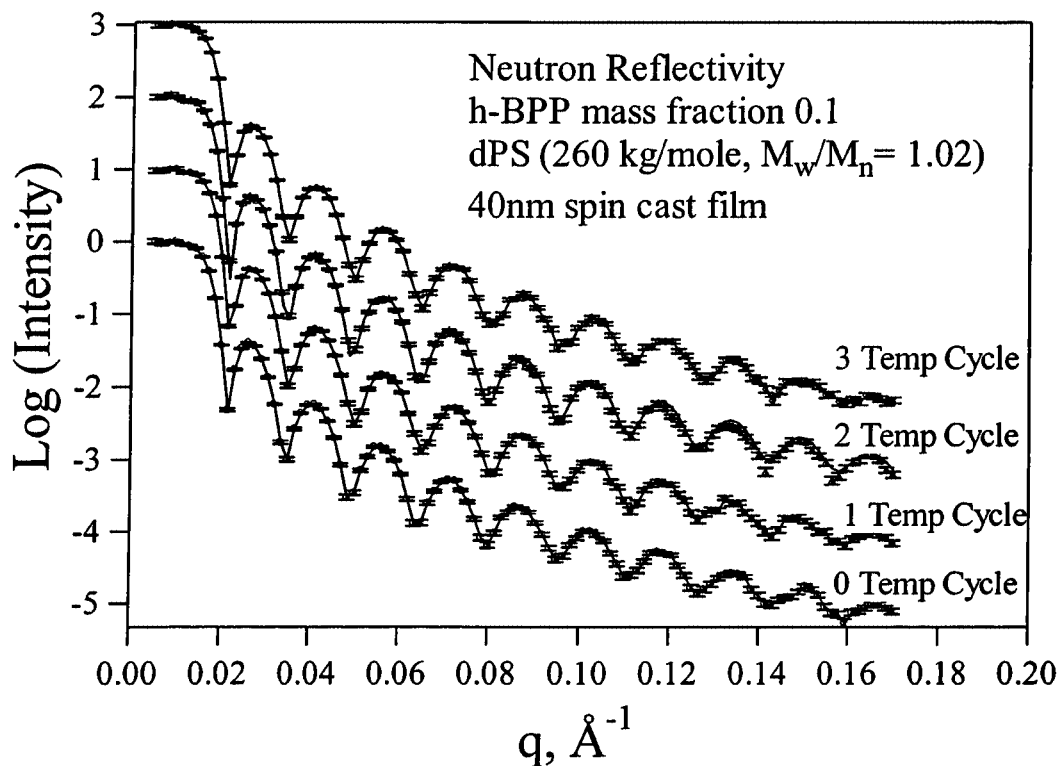


Fig. 3. Neutron Reflectivity curves. This is further illustrated in Fig. 3 by the neutron reflectivity intensity versus q data for 0, 1, 2, and 3 thermal cycles. These curves have been vertically shifted in one decade increments for clarity. These four curves can be superimposed to yield a single master curve. The solid lines are the calculated fits to the data using the parameters listed in Table 1.

polymer chains for the annealing at $T < T_g$. These annealed samples indicate that the probe is free to diffuse throughout the polymer matrix as expected and that there is no short time segregation of the probe to one of the interfaces. Additional SIMS determinations were performed for 1–4 thermal cycles of annealing. The SIMS profile for 4 cycles of annealing is also shown in Fig. 4. This data shows a small degree of segregation to both interfaces: the silicon interface and the free surface. The integrated area of the peaks at the Si interface and the free surface represent $4\% \pm 1\%$ and $2.5\% \pm 1\%$ of the total BPP volume fraction respectively. This is consistent with the X-ray reflectivity data. This small degree of segregation is below the sensitivity of the X-ray reflectivity experiment performed in this study. This data indicates that 93% of the chromophore is uniformly distributed throughout the film.

By using selective deuteration, combined with X-ray and neutron reflectivity techniques, the position of the BPP chromophore within the film can be determined. Additional evidence is provided by the SIMS results. These experiments have indicated only a small fraction of the probe is segregating ($10\% \pm 3\%$) during 4 thermal cycles of the sample. This assumption is based on four pieces of evidence. First, the roughness does not change in either the neutron or X-ray best-fit models as a function of the number of thermal cycles.

Second, the thickness does not change in either the neutron or X-ray best-fit models as a function of the number of thermal cycles. Third, the composition-sensitive Q_c^2 values employed in the fits to the neutron reflectivity data are consistent with the known initial homogenous composition of the film. Finally, the SIMS results demonstrate that after 4 thermal cycles, a small fraction of the chromophore has segregated to both of the interfaces with the majority of the chromophore uniformly distributed throughout the film.

Coefficient of Thermal Expansion (CTE)

The thickness of the polystyrene films, obtained from the best-fit model to the intensity versus q data collected at a specific temperature, is shown in Figs. 5a and 5b. The solid circles are the data collected upon heating, and the open circles are the data collected upon cooling of the film. The solid lines on this figure are the predictions for a bulk polystyrene film of equivalent thickness. The solid lines are calculated from the known values of the CTE for bulk polystyrene below T_g (glass) and above T_g (rubber) including a correction for Poisson's ratio. The data in Figs. 5a and 5b show that the coefficient of thermal expansion measured for the polystyrene film below the measured bulk T_g is equivalent to the prediction based on bulk glassy polystyrene measurements. The data collected above the bulk T_g show good agreement with the

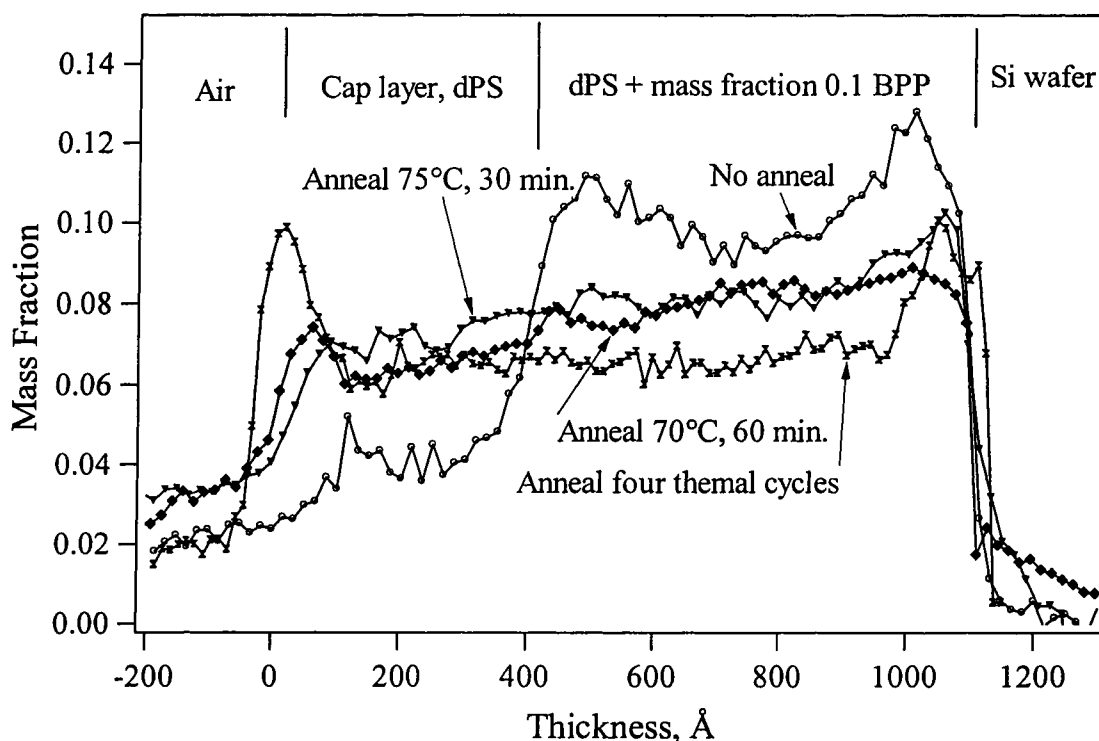


Fig. 4. Secondary Ion Mass Spectroscopy data. The volume fraction of BPP chromophore as a function of sample thickness is shown for four different annealing conditions: no annealing, 70°C for 60 min, 75°C for 30 min, and four thermal cycles. The BPP probe is clearly segregated in the no annealing sample, and is uniformly distributed in both the 70°C and 75°C annealed samples. The profile evident after four thermal cycles shows $10\% \pm 3\%$ of the integrated area has segregated into either the Si or free surface. This indicates that the majority of the chromophore is uniformly distributed throughout the film. The standard deviation of the mass fraction is 0.005.

predictions based on the bulk rubbery polystyrene. The transition between these two behaviors, glassy CTE to rubbery CTE, defined as the glass transition temperature, occurs at $(100 \pm 10)^\circ\text{C}$. The glass transition temperature of the polystyrene with BPP probe was determined independently by using a differential scanning calorimeter with a heating rate of $10^\circ\text{C}/\text{min}$ (calibrated versus Indium at the same heating rate). The resulting data exhibit an expected transition centered at 100°C (calculated by midpoint method).

The data presented in Fig. 5a (35 nm) and 5b (18 nm) for the polystyrene films are consistent with earlier independent fluorescence determinations of T_g (19). These two studies show that the T_g of ultra-thin polystyrene films supported on quartz do not exhibit thickness dependence, even though these films are on a size scale comparable to that of the polymer molecule.

The measurement of the CTE of ultra-thin polystyrene films by X-ray reflectivity and its direct correlation to a fluorescence probe technique links the fluorescence probe technique (sensitive to local dynamics) and the X-ray reflectivity technique (sensitive to the overall film material properties). Both these techniques report a thickness independent T_g of $(100 \pm 10)^\circ\text{C}$, further suggesting that both of these techniques are measuring the same process in this system.

These studies show that by shifting from a silicon (Si/SiOx) supported film to quartz supported film, no changes in the T_g behavior of the ultra-thin polymer films are observed. This is not an unexpected result. The studies that have shown a significant impact on the T_g due to changes in surface chemistry have significantly modified the surface energy of the substrates (5, 23). The transition from Si/SiOx to quartz does not represent a significant change in surface properties.

CONCLUSIONS

Selected deuteration of the polystyrene was used in conjunction with X-ray and neutron reflectivity to determine that the chromophore was not significantly segregating during thermal cycling. This observation was based upon no change in the roughness or thickness employed in the model best fits to either experimentally determined X-ray or neutron reflectivity intensity versus q data. Additional SIMS measurements confirm the lack of significant probe segregation.

The change in thickness of the film with temperature was found to be in good agreement with the bulk coefficient of thermal expansion predictions for both a 35 nm and 18 nm polystyrene films supported on quartz substrates in both the glassy and rubbery regions. Additionally, the transition between these two

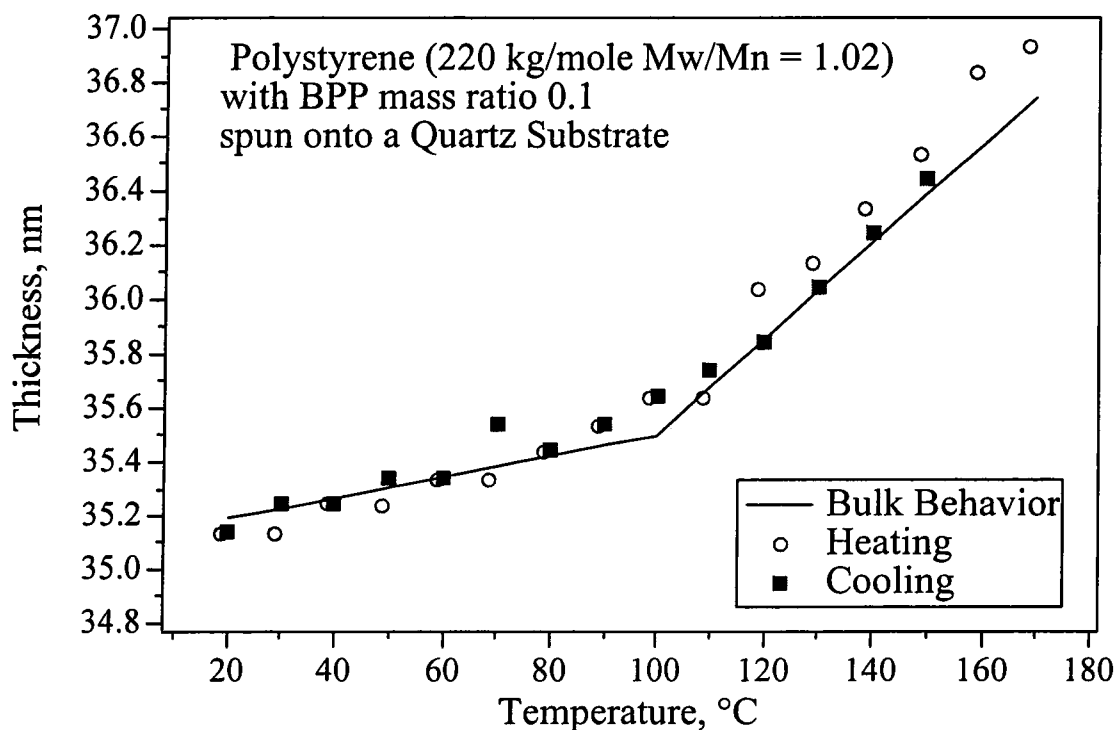


Figure 5a

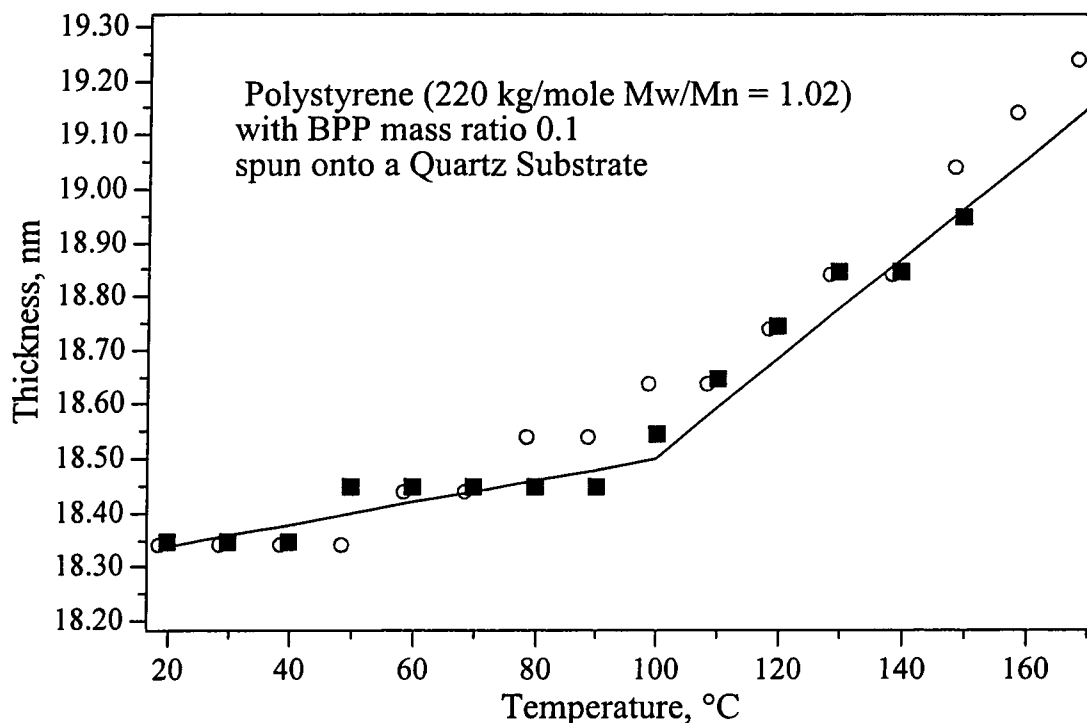


Figure 5b

Fig. 5. Coefficient of Thermal Expansion. The temperature dependence of the thickness of a polystyrene film spin on a quartz substrate is shown. The thickness was determined from the best-fit model prediction to the intensity versus q experimental data at each temperature. The open circles are the data obtained on heating and the filled symbols are obtained on cooling. The solid lines are the predictions based on the CTE of bulk polystyrene corrected for Poisson's ratio. The T_g is determined as the transition between the glassy and rubbery expansion values. This occurs at $(100 \pm 2)^\circ\text{C}$, which is equivalent to the observed bulk value for both the 35 nm (5a) and 18 nm (5b) polystyrene film. The bars on the data points represent the standard uncertainty of the data points.

regions of behavior occurred at $(100 \pm 10)^\circ\text{C}$, which is consistent with independent determinations of T_g for a similar sample and published literature results. This is also in agreement with both previously reported fluorescence determination of T_g (19) supported on quartz and X-ray reflectivity results supported on silicon wafers (5).

These results suggest that the differences between the previously reported local probe studies exhibiting no dependence on T_g as a function of film thickness (19) and local probe studies exhibiting a change in T_g with decreasing film thickness (16–18, 27, 28) are not attributable to the change from Si/SiO_x substrates to quartz substrates or the effect of probe segregation.

ACKNOWLEDGMENTS

C. C. W. would like to acknowledge the support of the NRC-NIST Postdoctoral Research Associates Program. The authors would also like to acknowledge helpful discussions with J. M. Torkelson, J. A. Forrest, J. R. Dutcher, C. Soles, E. Lin, G. B. McKenna and J. Douglas.

REFERENCES

1. S. Kawana and R. A. L. Jones, *Physics Review E.*, **63**, 021501 (2000).
2. E. Dalnoki-Veress, *et al.*, "Molecular Weight Dependence of Reductions in the Glass Transition Temperature of Thin, Freely Standing Polymer Films," *Physical Review E.*, **6303** (3), p. art. no. 031801 (2001).
3. S. Ge, *et al.*, "Shear Modulation Force Microscopy Study of Near Surface Glass Transition Temperatures," *Physical Review Letters*, **85** (11), p. 2340–2343 (2000).
4. Y. Pu, *et al.*, "Mobility of Polymer Chains Confined at a Free Surface," *Physical Review Letters*, **8720** (20), p. art. no. 206101 (2001).
5. D. S. Fryer, *et al.*, "Dependence of the Glass Transition Temperature of Polymer Films on Interfacial Energy and Thickness," *Macromolecules*, **34** (16), p. 5627–5634 (2001).
6. W. Wallace, J. H. vanZanten, and W. L. Wu, *Phys. Rev. E.*, **52**, R3329 (1995).
7. J. D. Keddie, R. A. Jones, and R. A. Cory, "Size-Dependent Depression of the Glass Transition Temperature in Polymer Films," *Europhysics Letters*, **27** (1), p. 59–64 (1994).
8. O. K. C. Tsui, T. P. Russell, and C. J. Hawker, "Effect of Interfacial Interactions on the Glass Transition of Polymer Thin Films," *Macromolecules*, **34** (16), p. 5535–5539 (2001).
9. R. S. Tate, *et al.*, "Extraordinary Elevation of the Glass Transition Temperature of Thin Polymer Films Grafted to Silicon Oxide Substrates," *Journal of Chemical Physics*, **115** (21), p. 9982–9990 (2001).
10. D. S. Fryer, P. F. Nealey, and J. J. de Pablo, "Thermal Probe Measurements of The Glass Transition Temperature for Ultrathin Polymer Films as a Function of Thickness," *Macromolecules*, **33** (17), p. 6439–6447 (2000).
11. Y. Grohens, *et al.*, "Some Relevant Parameters Affecting the Glass Transition of Supported Ultra-Thin Polymer Films," *European Physical Journal E.*, **8** (2), p. 217–224 (2002).
12. Y. Grohens, *et al.*, "Glass Transition of Stereoregular Poly(Methyl Methacrylate) at Interfaces," *Langmuir*, **14** (11), p. 2929–2932 (1998).
13. J. A. Torres, P. F. Nealey, and J. J. de Pablo, "Molecular Simulation of Ultrathin Polymeric Films Near the Glass Transition," *Physical Review Letters*, **85** (15), p. 3221–3224 (2000).
14. N. Lacevic, *et al.*, "Growing Correlation Length on Cooling Below the Onset of Caging in a Simulated Glass-Forming Liquid," *Physical Review E.*, **66** (3), p. art. no. 030101 (2002).
15. F. W. Starr, *et al.*, "What Do We Learn From the Local Geometry of Glass-Forming Liquids?" *Physical Review Letters*, **89** (12), p. art. no. 125501 (2002).
16. D. B. Hall, J. C. Hooker, and J. M. Torkelson, "Ultrathin Polymer Films Near the Glass Transition: Effect on the Distribution of A-Relaxation Times As Measured by Second Harmonic Generation," *Macromolecules*, **30**, 667–669 (1997).
17. D. B. Hall, R. D. Miller, and J. M. Torkelson, "Molecular Probe Techniques for Studying Diffusion and Relaxation in Thin and Ultra-Thin Films," *Journal of Polymer Science B. Polymer Physics*, **35**, 2795–2802 (1997).
18. C. J. Ellison, *et al.*, "Confinement and Processing Effects on Glass Transition Temperature and Physical Aging in Ultrathin Polymer Films: Novel Fluorescence Measurements," *European Physical Journal E.*, **8** (2), p. 155–166 (2002).
19. C. C. White, K. B. Migler, and W. L. Wu, *Polym. Eng. Sci.*, **41**, 1497 (2001).
20. J. A. Forrest, K. Dalnoki-Veress, and J. R. Dutcher, "Interface and Chain Confinement Effects on the Glass Transition Temperature of Thin Polymer Films," *Physical Review E.*, **56** (5), p. 5705 (1997).
21. C. W. Frank, *et al.*, "Structure in Thin and Ultrathin Spin-Cast Polymer Films," *Science*, **273**, (16 August), p. 912–915 (1996).
22. J. H. vanZanten, W. Wallace, and W. L. Wu, *Phys. Rev. E.*, **53**, R2053 (1996).
23. O. Kahle, *et al.*, "Glass Transition Temperature and Thermal Expansion Behaviour of Polymer Films Investigated by Variable Temperature Spectroscopic Ellipsometry," *Thin Solid Films*, **313**, 803–807 (1998).
24. B. N. Taylor and C. E. Kuyatt, *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*, 1995, National Institute of Standards and Technology.
25. Identification of a Commercial Product is Made Only to Facilitate Experimental Reproducibility and to Describe Adequately Experimental Procedure. In No Case Does it Imply Endorsement by NIST or Imply That it is Necessarily the Best Product for the Experiment.
26. S. A. Schwarz, *et al.*, "Studies of Surface and Interface Segregation in Polymer Blends By Secondary Ion Mass-Spectrometry," *Molecular Physics*, **76** (4), p. 937–950 (1992).
27. J. G. Victor and J. M. Torkelson, "On Measuring the Distribution of Local Free Volume in Glassy Polymers by Photochromic and Fluorescence Techniques," *Macromolecules*, **20**, 2241–2250 (1987).
28. K. E. Miller, R. H. Krueger, and J. M. Torkelson, "Mobility Sensitive Fluorescence Probes for Quantitative Monitoring of Water Sorption and Diffusion in Polymer-Coatings," *Journal of Polymer Science Part B-Polymer Physics*, **33** (17), p. 2343–2349 (1995).